

A Study of the Catalytic Hydration
of Ethylene Oxide to Ethylene Glycol

BY

LELAND McCULLOCH REED

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A STUDY OF THE CATALYTIC HYDRATION
OF ETHYLENE OXIDE TO ETHYLENE GLYCOL

by

Leland McCulloch Reed

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CERTIFICATE OF APPROVAL

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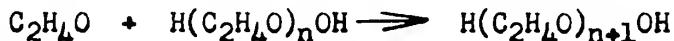
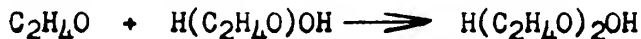
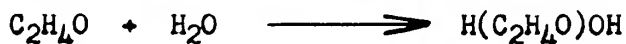
CHAPTER I

INTRODUCTION

Ethylene glycol has long been an important chemical. For several decades it has been the chief component of the permanent type anti-freezes and, in recent years, its uses have become more diversified. With the development of the process for the manufacture of ethylene oxide by direct oxidation of ethylene, the production of ethylene glycol has been diverted from the chlorohydrin process to the direct hydration of ethylene oxide. This resulted largely from the increasing demand for ethylene oxide as a base material for many products, including ethylene glycol, which stimulated research for cheaper means of production.

Ethylene oxide reacts readily with water to form ethylene glycol in either an acidic or basic solution and slowly reacts with water alone at elevated temperatures. The ethylene glycol in turn may react with more ethylene oxide to form diethylene glycol and this process repeated to form high polymers of high molecular weight.

These reactions may be represented as follows:



Industry has long accepted sulfuric acid as the standard catalyst for this conversion with apparently little interest in other catalysts.

It should be stated that sulfuric acid has proven most successful and

the meager information available in literature indicates that yields are high.

Although little information appears in the literature regarding the yields obtained in industry, data (1, 2) do exist which indicate that a 90% yield is about maximum. Since the higher glycols which constitute the major portion of the by-products have considerably less value, a more selective catalyst would contribute to an efficient process. In order to obtain the high yield of 90% it is necessary that a large excess of water, at least twenty times the theoretical amount, be present in the reaction. The separation of the excess water adds to the cost of the product. Perhaps with a suitable selective catalyst this large excess of water could be reduced with the ultimate being a theoretical ratio with no excess water. In existing processes where either a soluble acid or base is used, the product is contaminated with the catalyst which requires neutralization prior to distillation. The product is then contaminated with salt which is usually a relatively insoluble salt. Although most of the salt precipitates, mechanical separation is difficult and the salt remaining in solution produces scaling in the distillation equipment.

It is the purpose of this investigation to study the use of solid acids and bases in the form of ion exchange materials for the conversion of ethylene oxide to ethylene glycol. In this study there are four main objectives as follows:

1. Finding a catalyst which does not contaminate the products.
2. Finding a catalyst and establishing conditions which

accelerates preferentially the conversion to ethylene glycol.

3. Producing ethylene glycol in a more concentrated form.

4. Finding a permanent type catalyst.

Ion exchange materials in the acid or hydrogen form have successfully catalyzed many reactions, including ester hydrolysis and ester alcoholysis, which are reactions normally catalyzed by strong acids (3). With this knowledge, ion exchange materials in the acid form would be expected to accelerate the reaction in this investigation.

In all commercial processes the reaction between the oxide and water is conducted in the liquid phase. Several researchers have explored the vapor phase hydration without commercial success. This investigation will also include a study of the effect of phase condition on the reaction.

CHAPTER II

REVIEW OF LITERATURE

The increased demand for ethylene glycol in recent years has stimulated research in quest of more efficient manufacturing processes. Production figures for recent years are listed below.

<u>Year</u>	<u>Production in Pounds</u>
1947	226,673,000 (4)
1948	366,721,000 (5)
1949	439,746,000 (6)
1950	519,013,000 (7)

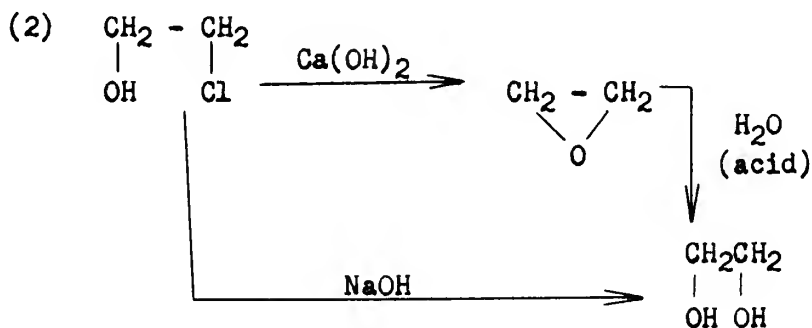
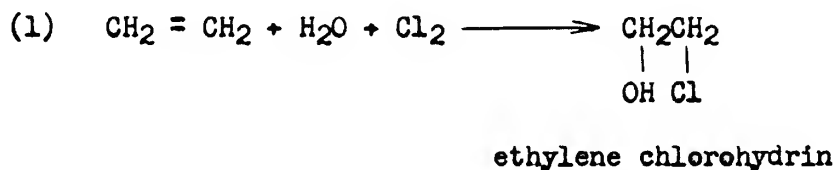
This is a notable increase and predictions are that production will continue to increase at an even greater rate. The desirable properties of ethylene glycol as an anti-freeze established it as a major chemical several decades ago. Since then, many diversified applications have added to the demand. The two active hydroxyl groups make it useful in the production of polymers for plastics and protective coatings. It is finding large use as a selective solvent in the petroleum industry in separating aromatics from other hydrocarbons. It serves as a raw material for many organic chemicals, such as glycol ether solvents, ethanolamines and dinitro glycol.

A. Manufacturing Processes

Ethylene glycol is produced commercially by several processes. The chlorohydrin process was developed around 1922 (8, 9) long before

the other processes received commercial importance. The process by direct oxidation of ethylene to ethylene oxide followed by hydration to ethylene glycol has only recently reached major importance. These two processes account for the most of the ethylene glycol produced in the United States today. The relative production figures of the two processes are not known. It was indicated in 1950 that the production by the direct oxidation process (10) greatly exceeded all other processes, while in 1949 it was reported that the chlorohydrin process (11) accounted for most of the production.

Reactions which illustrate the chlorohydrin process are as follows:



Ethylene is passed into a reactor containing a solution of hypochlorous acid maintained between 0°C. to 20°C. In continuous processes recycle hydrochlorin is also present in the hypochlorous acid, though the concentration of chlorohydrin must remain low, less than 8%. An

excess of ethylene is always employed to insure an ethylene chlorohydrin solution free of chlorine. The ethylene chlorohydrin may either be hydrolyzed directly to ethylene glycol employing sodium hydroxide or sodium carbonate or converted to ethylene oxide by reacting with milk of lime. The ethylene oxide thus produced is purified in a series of distillations and finally hydrolyzed to ethylene glycol. Hydrolysis can be conducted in a water solution in the presence of small amounts of sulfuric acid or at elevated temperatures and corresponding pressures.

In the direct oxidation process, ethylene is partially oxidized with air in a reactor bed containing a silver oxide catalyst (12). The ethylene oxide concentration from the reactor is low, usually from 1% to 5%. The oxide, being very soluble in cold water, is separated from the mixture by passing the gases through a water scrubber. The solution obtained is then heated and the reaction catalyzed by the addition of a small amount of sulfuric acid. Matignon et al (13) studied the reaction to determine the effect of the mole ratio of reactants, water and ethylene oxide, on the distribution of glycols, and concluded that a high mole ratio of water to ethylene oxide is necessary to obtain high yields. Davis et al (2) made a similar study on the uncatalyzed and on caustic catalyzed reaction and arrived at the same conclusion. In the catalyzed reaction it is necessary to keep the concentration of the catalyst very low, less than 0.1% for caustic and 1.0% for acid, in order to obtain yields near to the uncatalyzed values. Higher concentrations of catalyst

reduce the glycol and increase the higher glycol yields. While research has been done using the caustic catalyst, there is no evidence that it is used commercially.

The difficulties experienced in the separation of the soluble catalyst, mainly sulfuric acid, has resulted in considerable research to find a substitute that would not contaminate the products. Trihalogenated acetic acids have been reported as suitable catalysts (14). Decomposition of these acids on heating during the distillation eliminates the contamination, since volatile products are formed on decomposition. Amines have found similar use, although lower yields were reported (15). Smith and associates (16) attempted the vapor phase hydration of ethylene oxide and were successful with a silver oxide catalyst. However, the yield was low and the catalyst life was not adequate to attract commercial interest. A recent patent (17) reports the use of aluminum fluoride for catalyzing the reaction in the vapor phase with a yield of 90%, which is comparable to existing liquid phase hydration. Although it is too soon to know, this catalyst appears to have excellent commercial possibilities.

Another recently developed process (18, 19) starts with formaldehyde and carbon monoxide as base materials. Glycolic acid is produced in a continuous process by first dissolving formaldehyde in a solution of glycolic acid with sulfuric acid as a catalyst. This solution is then passed through a conversion chamber where it contacts carbon monoxide, with the formaldehyde being converted to glycolic acid. The acid is separated by crystallization and the remaining

solution recycled. Glycolic acid is then condensed to glycolic anhydride which is dissolved in an alcohol solvent, preferably ethylene glycol. Hydrogenation of this solution at a temperature between 195°C. and 215°C. and 900 atmospheres pressure converts the anhydride to ethylene glycol at yields near to 95%.

A process similar to the chlorohydrin process involves the complete chlorination of ethylene to yield ethylene dichloride followed by hydrolysis in the presence of a base. A weak base such as sodium carbonate contributes to the yield of ethylene glycol as opposed to a by-product, vinyl chloride which is favored when a strong base catalyst is used. This process has the disadvantage that twice the amount of chlorine is used in comparison to the chlorohydrin process.

Today the two competitive processes are the chlorohydrin process and the direct oxidation process. The initial plant cost for a direct oxidation process may be as much as double the cost of the chlorohydrin process. The yield of ethylene oxide by the chlorohydrin process is approximately 85% as compared to 60% for the direct oxidation. The advantage of the direct oxidation process is the negligible cost of the oxidizing agent air as compared to the high cost of chlorine, which usually amounts to slightly more than two pounds per pound of ethylene oxide. The economic balance then depends on equipment and ethylene oxide costs versus the cost of chlorine. Obviously this will vary with time and location. It is known that plants of both types are currently under construction, which is a clear indication that a delicate balance exists. An increased efficiency in the

conversion of ethylene to the oxide over the present 60% would greatly enhance the possibilities of the direct hydration process, and it is reasonable to expect that this low figure will increase as economic interests demand it.

B. Catalysis

Catalysts have been recognized for more than a century, though our study of catalytic phenomena is still more of an art than a science. However, the vast accumulation of knowledge on catalytic behavior over the past thirty years is rapidly converting this art into an exact science. In fact the organization of catalytic data today often makes sound predictions possible, and as basic knowledge of the mechanics of reactions is further revealed, it is quite possible that the random search for a perfect catalyst will be replaced by a logical selection.

By definition a catalyst is a substance which accelerates a reaction without becoming a part of the reactants or products. This alone does not tell the complete story. Catalysts do not supply energy to a reaction or alter the equilibrium of a reversible reaction. However, a catalyst may direct a reaction by selectively accelerating a particular reaction. Catalysts may have the characteristic of repeatedly entering into a reaction accompanied by regeneration; thus permitting small amounts of catalyst to transform large quantities of reacting materials.

Numerous theories have been postulated to explain the

phenomena of catalysis (20). The earliest theory suggested the alternate formation and decomposition of intermediate compounds between the catalyst and reactants, and there is evidence that many catalysts function in this manner. In the sequence of steps involving the intermediates, each step must have a lower free energy of activation than the direct reaction in an uncatalyzed reaction. Some catalysts are believed to have disruptive action on the reactant, which results from mere physical contact. The disruptive action is considered to be electrical in nature, thereby weakening the bonds and promoting more rapid reaction. Visible radiation is known to catalyze many reactions directly. Many other reactions are further catalyzed by the influence of a material catalyst which absorbs radiation energy at a high frequency and converts it to another frequency, usually in the infrared band, which is tuned directly to the reactants and therefore promotes reaction.

Resonance has been considered an important factor in catalysis. In order to have an interchange of energy and therefore reaction, resonance between the reactants must occur. In the case of homopolar bonding, the strength is determined by the spacing between atoms. A substance which can alter this spacing and thereby alter the frequency to coincide with another reactant can catalyze the reaction (21).

It is also considered that if the characteristic frequency of the catalyst is tuned to the frequency of the reactants, then a weakening of the bond in the reactant is effected thereby permitting reaction (22).

The phenomena of adsorption is associated with catalysis. Van der Waal's adsorption contributes toward increasing the concentration of reactants, thereby promoting the reaction. Of greater significance to catalysis is chemisorption, which has high heats of adsorption and moderate to large energies of activation. In conjunction with adsorption, highly active positions on the surface designated "active centers" (23) are considered the major influence. Supporting evidence to this theory is the fact that the heat of adsorption is initially high and decreases as more of the active centers are filled. Subsequent adsorption is more like that of the Van der Waal's type.

In spite of the vast amount of fundamental work done on catalysis, the problem of selecting a suitable catalyst often reverts to the trial and error solution. This trial and error technique may often be assisted by narrowing the number to a certain type, though this may be hazardous. With specific reference to the problem of hydrating ethylene oxide, the choice of ion exchange materials is a logical one. The knowledge that both acids and bases readily catalyzed the reaction was sufficient to lead one to consider these materials, which have exchangeable hydrogen and hydroxyl ions. Furthermore, references indicate that ion exchange materials are effective catalysts in similar reactions, such as the hydrolysis of esters (3).

C. Ion Exchange Materials

The application of ion exchange principles date back to the

time of Aristotle when sand filters were used for preparing potable water from sea and impure waters. However, Thompson and Way, two English agricultural chemists, are given credit for first recognizing the phenomenon of ion exchange (24). They reported treating soils with ammonium carbonate, with the ammonia being adsorbed and lime released.

It was established that the aluminum silicates were responsible for the exchange and from this developed the industrial uses of the siliceous ion exchangers. The limitations of the siliceous ion exchangers became evident as industrial applications broadened. This resulted in the discovery of sulfonated coal exchangers by Holmes and Adams (25, 26). Stable ion exchange resins of the sulfonic acid type and the polyamine type resins exhibiting anion exchange properties were observed by these men in 1935. The utility of ion exchange materials was quickly recognized by industry and academic institutions and research was stimulated in the field. Many new and unique applications were found for ion exchange materials and improved resins were developed. Within a relatively short period ion exchange materials have found use in separations, recoveries, catalysis, and deionization in addition to the well established process of water softening.

The theory and mechanism of ion exchange has received extensive study. Theories that are currently accepted are essentially in three groups: (1) the crystal lattice theory, (2) the double-layer theory, and (3) the Donnan membrane theory. All theories require that

the exchange of ions must satisfy the law of electroneutrality. They differ regarding the position and origin of the exchange site, though in all cases the site is an ionic grouping which forms electrovalent bonds with ions of opposite charge. The strength of the bond determines the ease with which the ion may be replaced in a manner analogous to dissociation of strong and weak electrolytes. The nature of the functional group between the substrate and exchangeable ion largely determines the strength of the bond which conforms to the strength of the acid or base formed. The stronger the acid or base, the weaker is the bond strength.

Cation exchange resins are highly cross-linked polymers containing polar anionic groups whose negative charge is balanced by the cation. They are essentially an electrolyte consisting of a large multivalent anion and numerous simple cations. The properties of the resin is largely determined by the polar functional group and is quite independent of the substrate anion.

The polar groups normally encountered in cation exchange resins are the following: sulfonic, phosphonic, carboxylic and phenolic. Their strength is dependent on the acid strength of the acid group. Therefore the acid strength of the exchange groups decreases in the following order (24): nuclear sulfonic - SO_3H , methylene sulfonic - $\text{CH}_2\text{SO}_3\text{H}$, phosphonic - $\text{PO}(\text{OH})_2$, carboxylic - COOH , and phenolic - OH . The order of the exchange affinities of the various ions follows the Hofmeister or lyotropic series in dilute solution. This order is not followed in non-aqueous media, at high

temperatures and at high concentrations.

Anion exchange resins are limited to the amine type resin. As with the cation exchange resins, the substrate is a highly cross-linked, insoluble resin, though ^{it} is a cation balanced by the mobile anions. Both strong and weak base anion exchange resins exist, which behave on titration in a manner similar to the corresponding base.

The inorganic ion exchange materials, both natural and synthetic, have found extensive use as catalysts. The zeolite minerals, which are crystalline silicates, have been used in the contact sulfuric acid process, petroleum cracking and refining, reductions, condensations and numerous other applications. The inorganic materials are generally used at temperatures above the destructive temperature of organic base catalysts.

The inorganic cation exchangers have found application (27) in a variety of organic reactions, such as esterification, acetal synthesis, ester alcoholysis, acetal alcoholysis, alcohol dehydration, ester hydrolysis, ester acidolysis and sucrose inversion. They serve essentially as an acid catalyst, though are insoluble and therefore present major advantages. Separation of the catalyst does not become a problem and therefore facilitates reuse. Their life without regeneration has been extremely long, which greatly reduces the cost of the catalyst in the processes. Contamination of products with the soluble acids often causes tedious and expensive purification processes. The resin catalysts have often been found to reduce the quantity of by-products normally occurring with soluble acids. Equipment costs

are generally reduced when an ion exchange resin is used as a catalyst, since corrosion is held to a minimum thus permitting cheaper materials of construction.

CHAPTER III

EQUIPMENT DESIGN, CONSTRUCTION AND OPERATION

A. Preliminary Investigation

1. Equipment for Preliminary Investigation

The lack of information in the literature on the use of ion exchange materials for catalyzing the reaction between ethylene oxide and steam or water suggested that a preliminary investigation would be advantageous. For this reason, a simple piece of equipment was designed and constructed with the knowledge that it would serve only to determine whether or not ion exchange materials were promising catalysts and with the intent that design data for more elaborate equipment would be available should the process appear worthy of further investigation.

The explosive nature of ethylene oxide, especially in the vapor phase, required that safety precautions be included in the design of the equipment. Fundamentally, the purpose of the equipment was to pass a mixture of ethylene oxide and water or steam through a catalyst bed and collect the products for analyzing. Based on this requirement and considering the nature of ethylene oxide, the equipment shown in Figure 1 was designed and constructed.

The reactor consisted of a $3/4$ inch by 2 foot glass tube which had a screen support placed in the bottom to retain the catalyst. This reactor was shielded by a $1/4$ inch steel plate with

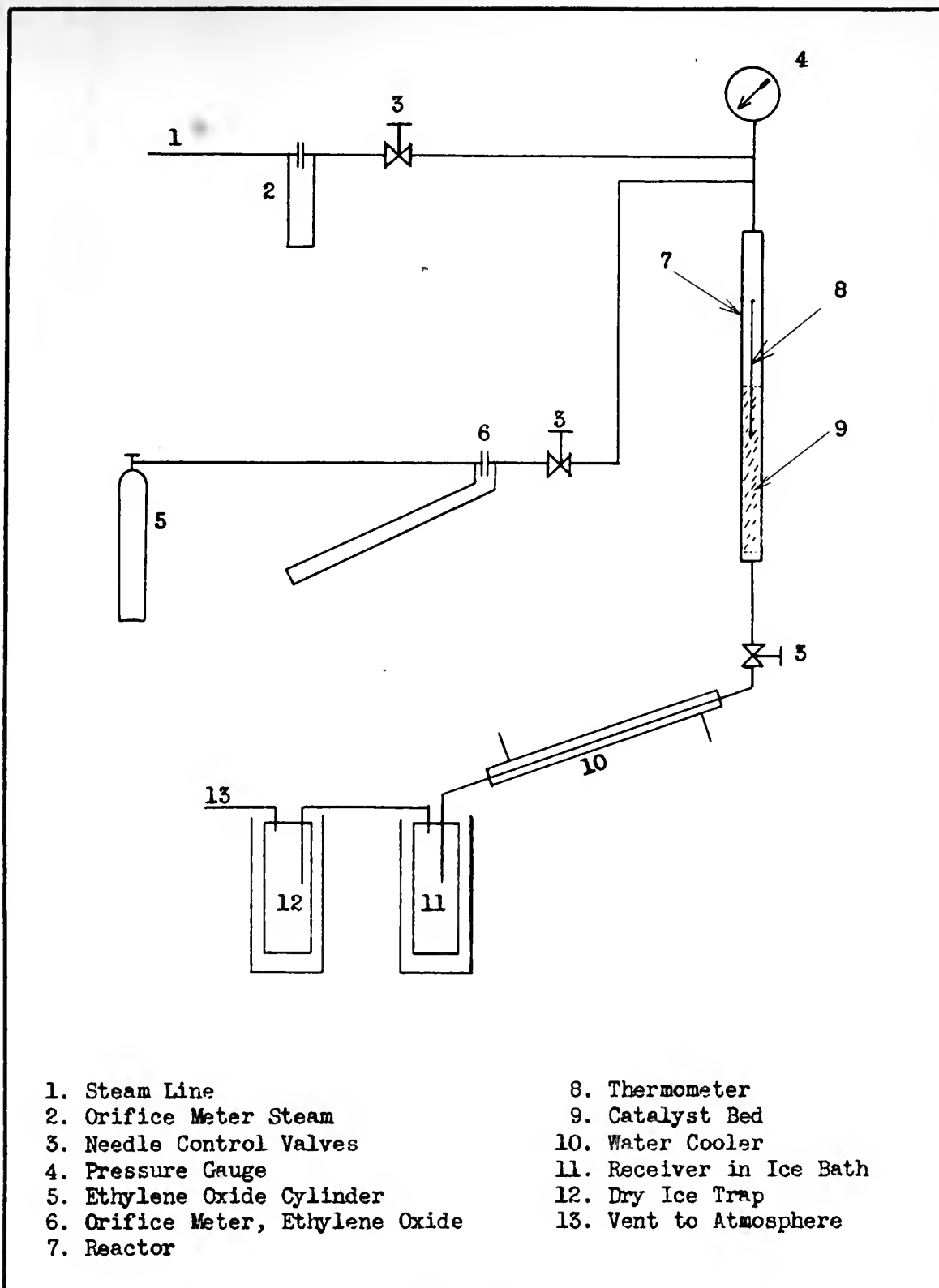


FIGURE 1

SCHEMATIC DIAGRAM OF EQUIPMENT FOR PRELIMINARY INVESTIGATION

a window of 3/4 inch Plexiglas for observation purposes. Rather than install thermocouples in the tube, a thermometer was inserted approximately two inches into the catalyst bed. Orifice meters were used to measure the flow of materials into the reactor. The usual type manometers were employed, with carbontetrachloride and mercury as fluids for the steam and ethylene oxide manometers respectively. The explosion hazard arising from ethylene oxide in contact with mercury called for shielding of the manometers with safety glass. The use of an inert gas blow-back was considered to prevent ethylene oxide from coming in contact with the mercury; however, this was discarded as being unnecessary considering the small quantity of ethylene oxide in the system at any time. The cylinder of ethylene oxide was placed outside the laboratory and shielded with sand as a personnel safety measure in the event of detonation. The equipment was therefore designed to withstand any detonation caused by the ethylene oxide in the system without danger to operating personnel.

Steam at 30 psig. was available in the laboratory. An entrainment separator was provided in the line to insure that water-free steam entered the orifice meter. The steam system was well lagged to minimize condensation in the meter and the line leading to the reactor; however, a source of heat was not provided to prevent partial condensation. Test runs indicated that total condensation occurred in the line and reactor at flow rates less than 100 grams per hour. Accepting this limitation, it was decided to operate at rates of approximately 200 grams per hour, which would provide steam

in the reactor of approximately 50% quality.

The wide choice in densities of suitable manometer fluids for steam made it possible to design the steam meter with reasonable accuracy. However, in the case of ethylene oxide, mercury is the only available fluid that does not readily dissolve ethylene oxide. With an orifice diameter of 0.025 inches, which was about the minimum size considered for mechanical reasons, and because of the possibility of becoming plugged with small particles of foreign material in the line, the differential pressure for flow rates of approximately 50 grams per hour is near 0.5 inch of mercury. The manometer was inclined at an angle of 20 degrees with the horizontal, but even this did not provide any high degree of accuracy. A differential reading of 1.5 inches of mercury corresponded to 62 grams per hour and, since the manometer could not be read accurately to less than 0.1 inch, it is evident that the manometer would serve only as a means of controlling the flow and quantitative measurements for yield purpose must come from analyses of the products.

The investigation was initiated during the winter months and the ambient temperature of the cylinder was not adequate to provide a working pressure of about 10 psig., which made it necessary to install a steam line about the cylinder to insure an adequate working pressure. The work continued into the summer months, which resulted in the ambient temperature of the cylinder exceeding the room temperature of the laboratory. This resulted in ethylene oxide vapors condensing in the lines, orifice and manometer and prevented operation.

The entire ethylene oxide system was traced with a 3/16 inch copper tubing and steam applied to maintain the temperature above that of the cylinder. The cylinder required a small amount of heating during operation as normal transfer of heat from the atmosphere was not sufficient to maintain a working pressure.

The limited range of operating conditions is evident from the design of this preliminary equipment. However, it served to establish the suitability of ion exchange materials for catalyzing the reaction and provided personnel with experience and data for the design of equipment to enable a complete study of the reaction.

2. Operating Procedure for Preliminary Investigation

The catalyst was prepared by three consecutive washings with 10% HCl, using two volumes of acid for each volume of catalyst. On each washing the acid was allowed to remain for five minutes before decanting. Thorough washing with distilled water followed the acid treatment. Run 11 deviated from this procedure by treating the catalyst with ten volumes of concentrated sodium chloride solution following the washing. All traces of salt were removed by washing with distilled water. This treatment replaced a portion of the hydrogen ions with sodium ions and reduced the activity of the catalyst. A thermometer was then inserted about two inches into the bed by loosening the bed with water and finally draining the water from the bottom of the reactor. The reactor was then assembled in the apparatus and was ready for operation.

The steam line was bled free of condensate and steam allowed

to pass through the reactor for approximately 30 minutes. Ethylene oxide was then introduced and the flow rates and reactor pressure brought to the desired values. To assure equilibrium conditions in the reactor, a sample was never collected until after conditions were constant, within the limits of control, for a period of 30 minutes. A sample was then collected over a period of about one hour or until a sufficiently large sample had collected to make a distillation analysis. Normally, the entire sample collected in the receiver immersed in ice. Only with those runs in which the sample contained a large amount of unreacted ethylene oxide was there an appreciable quantity of the oxide collected in the acetone-dry ice trap. However, the trap was always used as a safety precaution.

Data recorded during the runs were as follows:

1. Reactor pressure
2. Reactor temperature
3. Steam and ethylene oxide meter readings
4. Time

B. Pilot Plant Study

1. Equipment Design and Construction

Basically the pilot plant to complete the study of the reaction conformed to the design of the preliminary equipment. The system continued to be a flow process with the reactants passing down through the catalyst bed. The limited temperature and pressure range formerly obtained had to be extended. A temperature range from ambient

temperature to 400°F. was necessary. Pressures varying from 5 to 200 psia. were desired. These conditions precluded the use of laboratory steam or ethylene oxide vapor from a cylinder. Steam at this pressure was not available and ethylene oxide polymerizes readily when heated to 100°C., which is the temperature at a vapor pressure of 200 psia. The desired conditions suggested a displacement system employing an inert gas as the displacing medium. Nitrogen as recommended (28) for this purpose was used.

A schematic diagram of the pilot plant is shown in Figure 2. The water system consists of a four liter aluminum pressure vessel, a rotameter, a heating coil and the necessary control valves and fittings. All materials of construction up to the rotameter were of aluminum and from the rotameter on to the reactor materials were stainless steel No. 316.

The heating coil consisted of a ten foot length of 1/4 inch stainless steel tubing coiled in an oval shape about 6 inches by 12 inches. Three 600 watt flat electric heating units were placed adjacent to the coil and clamped in place with 1/4 inch Transite. Several layers of asbestos paper were installed between the heating unit and Transite to reduce heat losses and prevent the Transite from overheating. Two of the heating units were connected directly to a 110 volt source of power and the third supplied with a variable voltage autotransformer. A variable heating capacity from 0 to 1800 watts was therefore possible with this system.

The supply cylinder of ethylene oxide was inverted in a

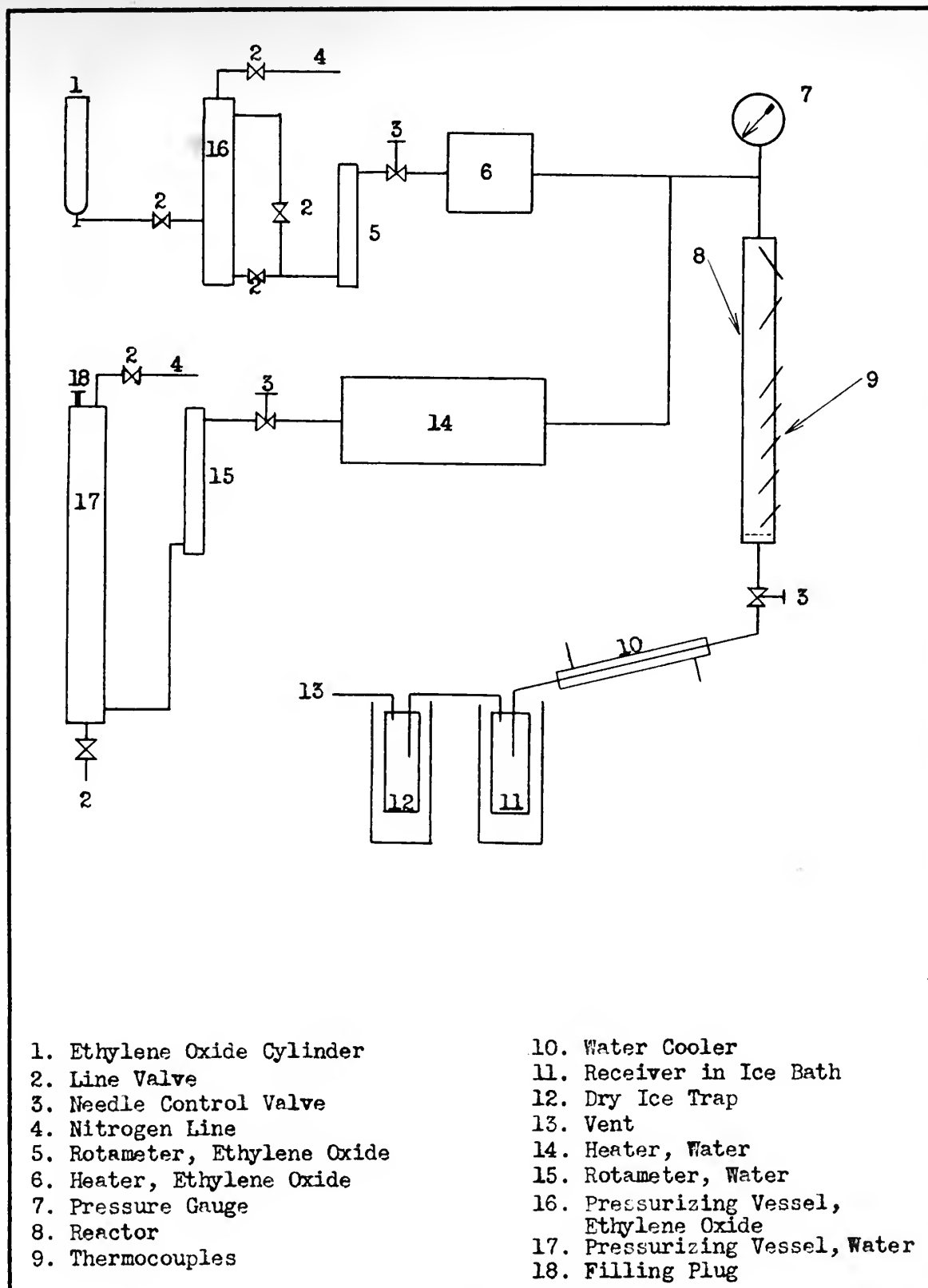


FIGURE 2

SCHEMATIC DIAGRAM PILOT PLANT

rack about thirty feet from the equipment. Barricading of this cylinder was not considered essential, as both the cylinder valve and line valve would be closed whenever the equipment was in operation. The ethylene oxide receiver was a steel pressure vessel of approximately 750 ml. capacity to which pressure could be applied with the compressed nitrogen. This receiver was well sandbagged in the event of an explosion. The arrangement of lines to the vessel to allow for filling and subsequent operation are shown in Figure 2. A photograph of the receiver with most of the sandbags removed is shown in Figure 3. The piping arrangement made possible the use of the rotameter as a sight glass to indicate when the vessel was full of liquid. All parts of the ethylene oxide system up to the control valve were of steel. The control valve, heating coil and connecting tubing and fittings were of stainless steel No. 316. This was necessary as water or steam could enter the ethylene oxide system up to the control valve when the oxide was not flowing.

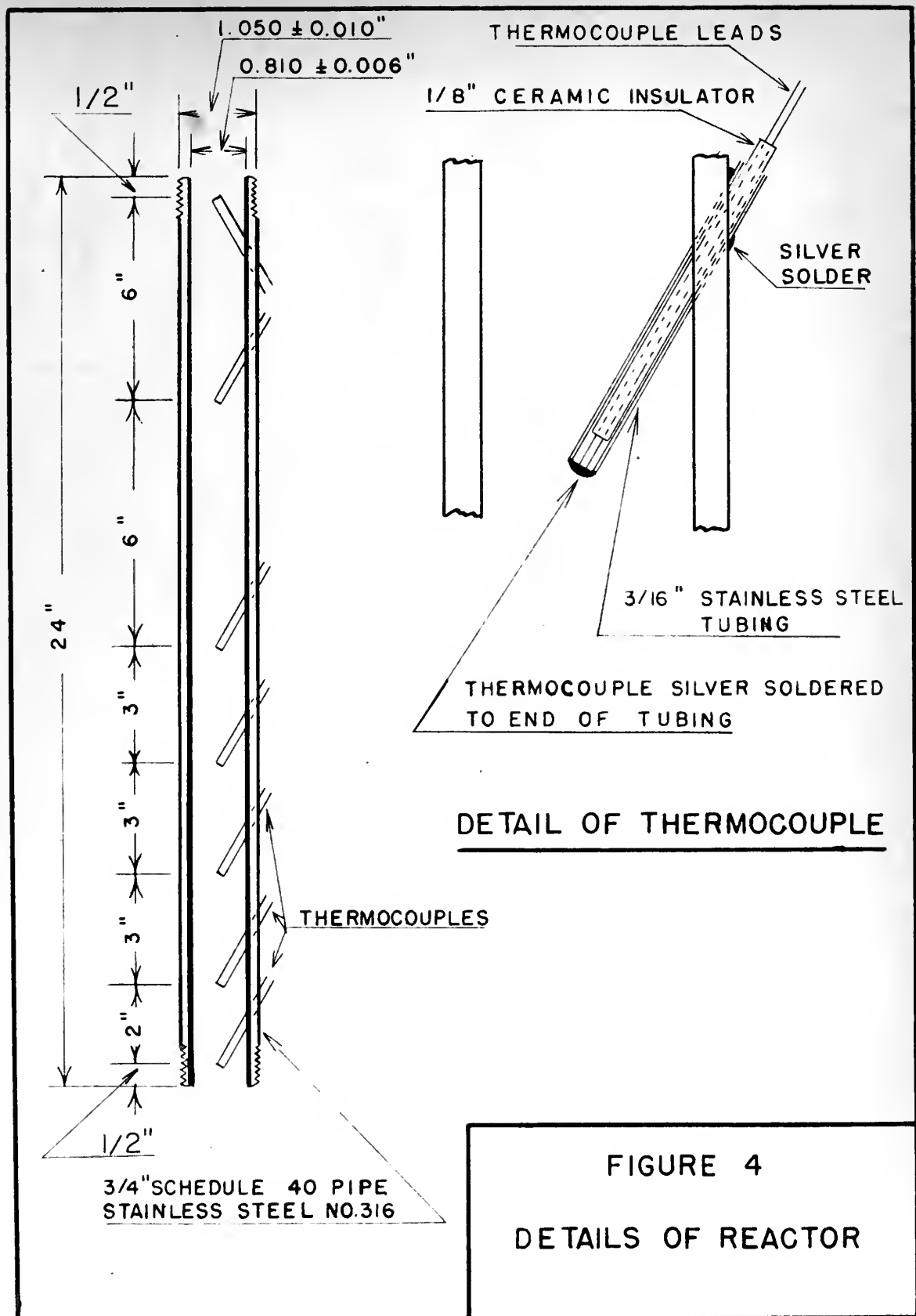
The heating coil for the ethylene oxide was similar to the water heating coil, though it consisted of a single 600 watt heating unit clamped against a four foot coil of 1/4 inch No. 316 stainless steel tubing. The coil was brazed to a piece of brass stock 4 inches in diameter by 2 inches in length in which a thermometer well and a thermo-regulator were installed. A variable voltage autotransformer was used to control the temperature with the thermo-regulator acting only as a safety device, should faulty operation allow the coil temperature to rise excessively.



FIGURE 3
VIEW OF ETHYLENE OXIDE RECEIVER

Check valves in either of the systems was unnecessary, as both the water and ethylene oxide receivers were pressurized with the same regulator, therefore preventing back-up into either system. The reactor consisted of a 3/4 inch by 2 foot Schedule 40 pipe of No. 316 stainless steel with a fitting on the top to enter the ethylene oxide and water lines. Seven copper constantan thermocouples were installed in the reactor center as indicated in Figure 4. The thermocouple wells were installed at an angle of 25° with the axis of the reactor, which provided a ratio of length to the diameter of the well of approximately 5:1. With this ratio, temperature gradients in the well can be neglected. Asbestos covered No. 20 B&S Chromel A wire was wound about the entire length of the reactor to provide temperature control. The electric coil was designed for 750 watts at 110 volts, and controlled with a variable voltage autotransformer. Because of high heat losses at the reactor heads, it was necessary to install heating coils about these to provide uniform temperature control. These coils were connected in series with the bottom coil having 200 watts and the top coil 150 watts at 50 volts. Here also, control was by means of a variable voltage autotransformer.

Temperatures in the reactor were measured with the thermocouples, using a Wheelco Model 300 Potentiometer. Multiple contact plugs were used in the thermocouple leads to facilitate disassembly of the reactor unit. A selector switch was installed on the control panel for selecting the various positions in the reactor bed. Calibration of the thermocouples indicated an error of less than 1°F.,



which is approximately the precision of the potentiometer, and therefore no attempt was made for greater precision.

The products leaving the reactor first passed through a water cooled heat exchanger and then into a flask receiver submerged in crushed ice. To assure no loss of ethylene oxide, the flask receiver was vented to a trap immersed in dry ice acetone solution which maintained a temperature of -78.5°C .

Figure 5 is a photograph showing the pilot plant and auxiliary equipment to the left and the analytical distillation apparatus to the right.

2. Pilot Plant Operating Procedure

a. Catalyst Preparation - Preparation of the catalyst continued the same as in the preliminary investigation when used in the acid or hydrogen form. Run 22A was made with the catalyst in the sodium form. For this run the catalyst was washed three times with two volumes of 10% NaOH per volume of catalyst for each washing. This was followed by thorough rinsing with distilled water. Rather than measure the depth of catalyst in the stainless steel pipe reactor, it was found to be more convenient to wash the desired volume of catalyst into the reactor. In all cases, the volume of catalyst was measured after freely settling in distilled water, which was the initial condition of the catalyst in the reactor. Careful checks on the depth of catalyst before and after a run was made indicated only slight settling with the exception of the anion exchange resin, Permutit S. Normal settling of all the catalysts did not exceed

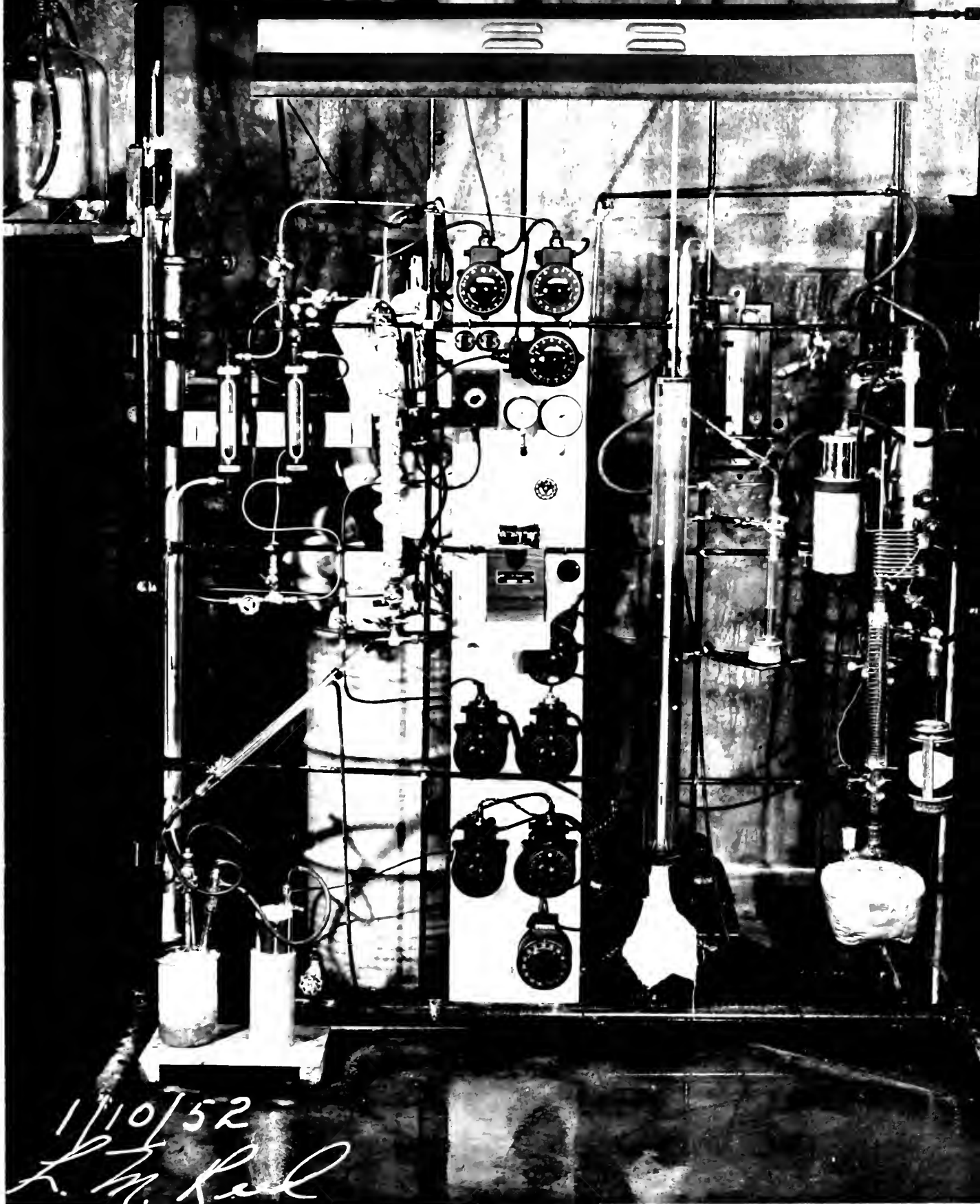


FIGURE 5
VIEW OF PILOT PLANT AND
ANALYTICAL APPARATUS

1/2 inch when operating temperatures remained below 250°F. On the few runs where the temperature ranged above 300°F. with the Permutit Q, settling was found to be greater, increasing to approximately 1½ inches. The Permutit S softened excessively at a temperature of 210°F. and actually started sealing the bed. This in turn caused the pressure drop through the bed to rise and greatly compressed the catalyst. In the only successful run on this catalyst, the bed settled approximately three inches.

b. Charging - Distilled water was used for all runs. The pressure in the water receiver was released, the filling plug removed and water siphoned into the receiver. After replacing the plug, nitrogen pressure was applied. The ethylene oxide was charged by first venting the receiver to atmospheric pressure and then opening the valve from the inverted cylinder of ethylene oxide. Since both the receiver and cylinder were normally at room temperature, it was necessary to continually vent the receiver to maintain a pressure differential. This was accomplished by closing the valve in the bottom line from the receiver and opening the valve in the top line, of which both entered the rotameter. In this manner ethylene oxide vapor vented through the rotameter and out the reactor, which permitted one to determine visually when the receiver was filled; that is, when liquid started passing through the rotameter. After charging, the valves were again adjusted to cause the liquid to pass from the bottom of the receiver and nitrogen pressure applied.

c. Starting Procedure - Prior to starting a run, the

operating conditions, temperature, reactor pressure and flow rates were established. The nitrogen pressure applied to ethylene oxide and water was adjusted to give a differential pressure^{of} approximately 20 psi. This differential was found to be near optimum, as higher differentials caused the control valves to be excessively sensitive to control and lower differentials permitted slight variations in the reactor pressure to cause excessive variations in flow rates. Uniform flow rates under the best conditions were difficult to obtain. When vaporizing either of the entering materials, momentary large fluctuations in the back pressure was caused by the intermittent flashing of liquid. When operating conditions permitted the ethylene oxide and water to enter the reactor in the liquid phase, these fluctuations were greatly reduced. Ethylene oxide would therefore flash in the reactor when contacted by the hot water and this type of vaporization in the larger space provided by the reactor proceeded without excessive fluctuations in pressure.

Control of the ethylene oxide was made even more difficult when operating at pressures of 10 psig. and below. At these pressures, the pressure drop across the control valve caused cooling of the valve by vaporization, which in turn caused the residue dissolved in the ethylene oxide, likely carbo waxes, to precipitate. This precipitate accumulated in the valve causing a continual decrease in flow rate. A small electric heater was applied to the valve which greatly improved the control; however, when operating at pressures below atmospheric, control of the flow rate was very poor. The heating of the valve was

critical as too high a temperature would cause the ethylene oxide to flash on the high pressure side while too low a temperature permitted precipitation.

In starting a run, the water was turned on to any high rate and the electric power to steam coil and reactor adjusted to a value considerably in excess of what might be the final value. In this manner, the reactor would be brought to near operating temperature in a minimum of time, which would normally be about thirty minutes, depending on the desired temperature.

When the desired temperatures in the reactor were attained, the ethylene oxide was started, and all flow rate and power settings readjusted. With continuous care, it was possible to bring the operation to equilibrium conditions in about an hour. After the system had been in equilibrium for thirty minutes, a sample was taken by collecting the product over a period of time, ranging from forty-five minutes to several hours, depending on the flow rates. A sample was collected in a flask which could be transferred to the analytical distillation columns, thus eliminating any possible error that might arise were the sample transferred from one receiver to another. Care was always taken to immerse the receiver in an ice bath and the trap in a dry ice acetone solution.

Data recorded during the runs are the following:

1. Millivolt reading from each of the seven thermocouples
2. Ethylene oxide and water rotameter readings
3. Time
4. Reactor pressure

C. Analytical Procedure

The products were analyzed by means of fractional distillation. Other methods were considered, though it was concluded that distillation was a satisfactory method and the only practical method available. Chemical analytical methods are much too time consuming when considering the number of likely components in the products. Even with the fractional distillation, it required from eight to ten hours to analyze a run as compared to two or three hours to make the run.

In the preliminary investigation a single distillation column was used. It consisted of a 20 mm. column packed with stainless steel knitted wire mesh to a height of 35 cm. A distillation head was constructed to provide suitable adjustment of the reflux ratio. Since tap water did not provide sufficient cooling for refluxing the ethylene oxide, it was necessary to construct a refrigeration system which circulated a solution of dry ice and acetone through the condenser. In addition, it was necessary to wind a copper tubing about the column head and circulate a solution of dry ice and acetone through it to prevent superheating of the vapors by the atmosphere. The dry ice and acetone solution circulated in series through the copper coil, condenser and the reservoir of solution. Natural convection caused by heating in the coil and condenser was adequate to maintain a flow of cooling solution. The refrigeration system was necessary until the temperature of distillation was well above the temperature of cooling water. This always came between the ethylene oxide and water fractions.

The 20 mm. column proved to have too much column hold-up per theoretical plate for obtaining sharp cuts between the glycols. Rather than go to larger samples to improve the accuracy of analyses, a smaller column was used for the final work. This was a 12 mm. Todd column as described by Todd (29), with a packing of 1/8 inch glass helices.

Samples from some of the runs produced distillation curves that were difficult to interpret. A considerable quantity would distill over in the temperature range between 100°F. and 212°F. On dehydrating this cut, it was found to be largely water, although appreciable quantities of materials other than water occurred in some of the runs. The procedure for analyzing these intermediate cuts consisted of dehydrating with anhydrous magnesium sulfate, washing the mixture several times with anhydrous ethyl ether and finally evaporating the ether to obtain the quantity of material other than water which are termed intermediates in this study. Dioxane was identified in this material; however, there was never sufficient material to make a distillation analysis. Dioxane forms an azeotrope with water containing 48 mole per cent dioxane boiling at 87.82°C., which may account for the large percentage of water in this cut. In those runs where the yields were high, negligible amounts of intermediates were found.

A minor change in procedure was made on those runs following No. 3A. It was found to be exceedingly difficult to bring over the small amount of water remaining in the sample after transfer to the vacuum still. The large differential in the boiling temperatures of

water and ethylene glycol would indicate an easy separation. However, a smooth distillation was virtually impossible as the water would flow from the condenser and column head intermittently. When a few drops of water would pass from the cold to the hot region in the column, a small explosion would result, often blowing the glass helicies completely through the condenser. Temperatures would range between the boiling points of water and ethylene glycol at the operating pressure with no take off. To avoid this difficulty, the small amount of water remaining in the sample at the time of transfer to the Todd column was evaporated directly without fractionation. The sample was evacuated to a pressure of 20 mm. of Hg. and heated to a temperature about 20°C. below the boiling point of glycol. Normally about 10 ml. of water was removed. To justify this procedure 10 ml. of water was added to approximately 60 ml. of glycol and the water removed. The quantity of water obtained checked within 0.1 gram in all cases. This revision greatly facilitated the routine of analyses and improved the accuracy of the results.

All fractionations were made at atmospheric pressure through the water cut and vacuum applied for the glycol cuts. In general, an absolute pressure of 20 mm. of Hg. was used, except on a few of the runs in the preliminary investigation. In those cases, the vacuum was produced by a water pump which would only produce an absolute pressure of 25 to 27 mm. of Hg.

In analyzing the runs of the preliminary investigation, the samples were not weighed at any time. Since glycerol was used as a

chaser, there was no means of determining the amount of glycols higher than the dimer. At that time they were considered to be negligible, though further work proved this not so. Therefore, in the final study, the original sample and the sample at transfer to the Todd column, which consisted of only the glycols, were weighed. The fractionation of the glycols was taken through the diethylene glycol fraction, and difference in weight between the sample at transfer and the glycol and diethylene glycol was assumed to be higher glycols.

Since a complete analysis of all the products was not made, it was necessary to make certain assumptions before the percentage yield and percentage conversion could be calculated. It was assumed that weight ratio of ethylene oxide to intermediates was one to one. This is reasonable, as the two most likely compounds in this fraction, dioxane and methyl dioxolane, each have a weight ratio of one to one with ethylene oxide. Dioxane is the cyclic dimer of ethylene oxide and methyl dioxolane is the cyclic acetal of ethylene glycol and acetaldehyde. For the higher glycols, the weight ratio of ethylene oxide to glycols was based on triethylene glycol. This is a ratio of 1:1.137. Since the ratio for the higher glycols does not vary appreciably from this, as well as the fact that they constitute a small percentage of the total ethylene oxide, this is a sound assumption. With these two assumptions it was possible to compute the total equivalent ethylene oxide in the samples.

CHAPTER IV

RESULTS

A. Preliminary Investigation

The results of the preliminary investigation are summarized in Table I. This work was of an exploratory nature and served only to establish the utility of ion exchange resins in catalyzing the reaction between ethylene oxide and water. The temperature and pressure was not varied throughout these runs, remaining at 225°F. and 20.0 psia., respectively. It is noted that all ion exchange materials tried catalyzed the reaction to varying degrees, as contrasted by negligible conversion with sand and an open reactor. The analytical procedure used in the preliminary work would not detect conversions under about 5%. These are listed as nil in Table I.

B. Final Study

The results of the final study are summarized in Tables II through V. The reactor pressures are pressures measured in the upstream side of the catalyst bed. In all cases except Run 19A, the pressure drop through the bed was small, in the order of one pound per square inch. In Run 19A the downstream side of the catalyst bed was open to atmospheric pressure so the pressure drop across the bed is the gage pressure.

The space velocity term used in the table is a modified term or mass space velocity, mass per unit volume of catalyst per

TABLE I
SUMMARY OF DATA FROM PRELIMINARY INVESTIGATION

Run No.	1	2	3	4	6	7	8	9	10	11
Catalyst	Zeo-Karb H-form	Zeo-Karb H-form	None	Sand	Permutit Q H-form	Dowex 50 H-form	Permutit Q H-form	Permutit Q H-form	Permutit Q H-form	Permutit Q Na & H-form
Bed Depth, inches	12	12	--	12	6	6	12	12	12	12
ml. of catalyst	90	90	--	90	45	45	90	90	90	90
Temp °F. 2" from top	225	225	225	225	225	225	225	225	225	225
Reactor Pressure psia.	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Mass Space Velocity gr./hr. x ml.										
Total	4.0	2.9	3.1	2.9	3.8	3.3	3.2	3.2	3.3	3.9
C ₂ H ₄ O	0.59	0.60	0.58	0.58	0.85	0.58	0.47	0.47	0.50	0.67
H ₂ O	3.4	2.3	2.5	2.4	3.0	2.7	2.7	2.7	2.8	3.2
Mole Ratio H ₂ O/C ₂ H ₄ O	14.1	9.4	10.4	11.8	8.8	11.4	14.2	14.2	13.7	11.8
% Conversion	71.3	51.9	nil	nil	65.5	40.8	95.4	95.7	90.0	39.5
% Yield										
Ethylene Glycol	80.2	87.0	--	--	93.5	79.4	72.4	78.5	78.7	83.0
Diethylene Glycol	19.8	13.0	--	--	6.5	20.6	27.4	21.5	21.3	17.0

TABLE II
PILOT PLANT DATA

Run No.	12	13	14	15	16*	1A	2A	3A	4A
Catalyst	Permutit Q H-form	Permutit Q H-form	Zeo-Karb H-form	Permutit Q H-form	Sand	Permutit Q H-form	Permutit Q H-form	Permutit Q H-form	Permutit Q H-form
Bed Depth, inches	12	12	12	12	24	12	12	12	12
ml. of catalyst	100	100	100	100	200	100	100	100	100
Temp °F.									
Top	206	207	230	235	215	207	213	230	238
Middle	226	215	249	271	208	219	215	240	284
Bottom	226	221	268	271	206	225	225	244	320
Reactor Pressure psia.	20.0	20.3	20.0	20.5	20.0	20.0	20.0	25.0	25.0
Mass Space Velocity gr./hr. x ml.									
Total	3.1	6.0	5.5	5.7	3.1	6.0	9.3	5.8	5.7
C ₂ H ₄ O	0.40	0.90	0.98	0.73	0.47	0.75	1.23	0.79	0.85
H ₂ O	2.7	5.1	4.5	5.0	2.6	5.3	8.1	5.0	4.9
Mole Ratio H ₂ O/C ₂ H ₄ O	16.4	14.1	11.6	17.1	13.4	17.3	16.0	15.4	14.0
% Conversion	97.3	61.4	55.7	73.5	7.6	69.8	47.6	57.8	41.9
% Yield									
Ethylene Glycol	84.5	81.4	45.7	47.8	---	82.0	74.0	59.7	50.5
Diethylene Glycol	7.2	9.1	11.6	19.5	---	9.4	7.9	25.2	20.8
Higher Polymers	8.3	9.5	42.7	32.3	---	8.5	18.0	14.9	13.2
Intermediates**	---	---	---	---	---	---	---	---	15.5

* Run 16 was not analyzed because of the small conversion.

** Analyses on Runs 3A and before did not include those products boiling between 100°F. and 212°F., termed "intermediates".

TABLE III
PILOT PLANT DATA

Run No.	5A	6A	7A	8A	9A	10A	11A	12A	13A
Catalyst	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form	Permutit H-form
Bed Depth, inches	12	12	12	12	12	12	12	12	12
ml. of catalyst	100	100	100	100	100	100	100	100	100
Temp °F.									
Top	290	198	213	212	217	209	204	177	214
Middle	291	228	225	242	238	234	205	178	220
Bottom	311	238	232	247	248	270	210	180	221
Reactor Pressure psia.	20.0	25.0	25.0	25.0	30.0	45.0	16.0	10.0	20.0
Mass Space Velocity gr./hr. x ml.									
Total	5.4	5.3	4.4	2.6	5.6	5.6	5.3	5.2	5.2
C ₂ H ₄ O	0.62	0.71	1.37	0.83	0.85	0.89	0.83	0.83	0.84
H ₂ O	4.8	4.6	3.0	1.8	4.8	4.7	4.5	4.4	4.4
Mole Ratio H ₂ O/C ₂ H ₄ O	18.7	15.5	5.4	5.3	13.8	12.8	13.2	13.0	12.9
% Conversion	41.6	93.6	58.3	97.0	97.5	98.6	40.4	16.6	63.2
% Yield									
Ethylene Glycol	61.0	81.6	68.2	52.5	75.2	70.5	77.6	82.5	76.5
Diethylene Glycol	20.0	13.1	16.0	22.2	14.1	14.0	9.2	9.7	12.7
Higher Polymers	---	5.3	15.7	19.7	7.0	11.9	10.0	7.8	9.1
Intermediates	19.0	---	---	5.8	3.7	3.6	3.2	---	1.7

TABLE IV
PILOT PLANT DATA

Run No.	14A	15A*	16A**	17A	18A	19A	20A	21A	22A**
Catalyst	Permutit Q H-form	Permutit Q H-form	Permutit H H-form	Zeo-Rex H-form	Duolite C-60 H-form	Permutit S OH-form	Zeo-Rex H-form	Zeo-Karb H-form	Permutit Q Na form
Bed Depth, inches	12	12	12	12	12	12	12	12	12
ml. of catalyst	100	100	100	100	100	100	100	100	100
Temp °F.									
Top	292	324	215	207	194	182	194	194	196
Middle	303	331	214	215	206	202	198	206	194
Bottom	302	330	213	220	210	211	202	212	192
Reactor Pressure psia.	65.0	95.0	20.0	20.2	17.0	18.0- 29.5	15.5	15.7	15.5
Mass Space Velocity gr./hr. x ml.									
Total	5.4	5.7	5.2	4.2	4.8	4.6	5.2	5.1	5.1
C ₂ H ₄ O	0.81	0.83	0.85	0.72	0.76	0.49	0.97	0.90	0.91
H ₂ O	4.6	4.9	4.4	3.5	4.0	4.1	4.2	4.2	4.2
Mole Ratio H ₂ O/C ₂ H ₄ O	14.0	14.0	12.5	11.8	12.8	21.0	10.5	11.5	11.1
% Conversion	100.0	100.0	7.2	63.5	86.4	77.6	25.3	91.1	3.9
% Yield									
Ethylene Glycol	67.2	59.0	---	78.0	86.0	53.0	77.5	76.0	---
Diethylene Glycol	24.4	---	---	9.3	11.8	29.8	15.0	18.1	---
Higher Polymers	4.3	---	---	10.4	2.0	17.2	7.5	5.9	---
Intermediates	4.0	---	---	2.3	---	---	---	---	---

* Decomposition occurred during distillation after the ethylene glycol cut, which prevented a complete analysis of Run 15A.

** Runs 16A and 22A were not analyzed because of small conversions.

[illegible]

unit time. As usually defined, space velocity is the volume of feed per unit volume of catalyst per unit time. In the heterogeneous system existing in most of the runs, the volume of feed has little significance and it was considered that the mass term would be more useful. The percentage conversion is the percentage of ethylene oxide in the feed which is converted to other products. The percentage yield is the percentage ratio of the moles of ethylene glycol formed per mole of ethylene oxide reacted. This term is sometimes called "selectivity", though the percentage yield will be consistently used in this discussion.

Detailed data on the catalysts are given in Appendix I.

1. Phase Conditions

Runs 14, 15, 4A, 5A, 5B are the results of numerous attempts to operate entirely in the vapor phase. Assuming the materials obey Raoult's Law and based on the composition of the sample analyzed, all these runs would be entirely in the gaseous phase. Excessive and uncontrollable temperatures occurred when the ethylene oxide was first admitted to the reactor. Since the reactor was heated and had superheated steam passing through prior to entering the ethylene oxides, there was no liquid available to prevent temperature increases. It was finally discovered that this large temperature rise occurred only with a fresh catalyst, and that previous conditioning of the catalyst by operating in the liquid phase would then permit operation in the gaseous phase up to a temperature of about 325°F. This is evidence that an initial reaction occurs which is highly exothermic, perhaps chemisorption of ethylene oxide on the surface of the catalyst. A

highly exothermic reaction would pass undetected in a liquid phase reaction as the heat released would be absorbed in vaporizing a portion of the liquid, thus remaining at a constant temperature.

It is noted that the yields are low in all gas phase runs, ranging from 41.6% to 50.5%. Because of the poor results obtained when operating in the vapor phase, the remainder of the work was done at temperatures and pressures that established a heterogeneous system of vapor and liquid phases. The preliminary investigation indicated that Permutit Q in the hydrogen or acid form was the most promising catalyst from the standpoint of both yield and conversion. Sulfonated coal, Zeo Karb, in the hydrogen form gave results very near to the Permutit Q; however, the decision was made to conduct a detailed study only on the Permutit Q. This study consisted of establishing the effect of temperature and pressure, mole ratio and mass space velocity on the percentage yield and percentage conversion.

2. Combined Effect of Temperature and Pressure

The combined effect of temperature and pressure is shown in Figure 6. Other variables, mole ratio and space velocity, were held constant and the temperature varied from 180°F. to 330°F. The temperatures plotted are bottom temperatures in the catalyst bed. This position was chosen as the temperature and pressure more nearly followed the relationship of temperature and pressure for saturated steam. Also, the bottom temperature more nearly represented the overall reactor temperature than any other position. The pressures corresponded closely to the saturated steam pressures. The space

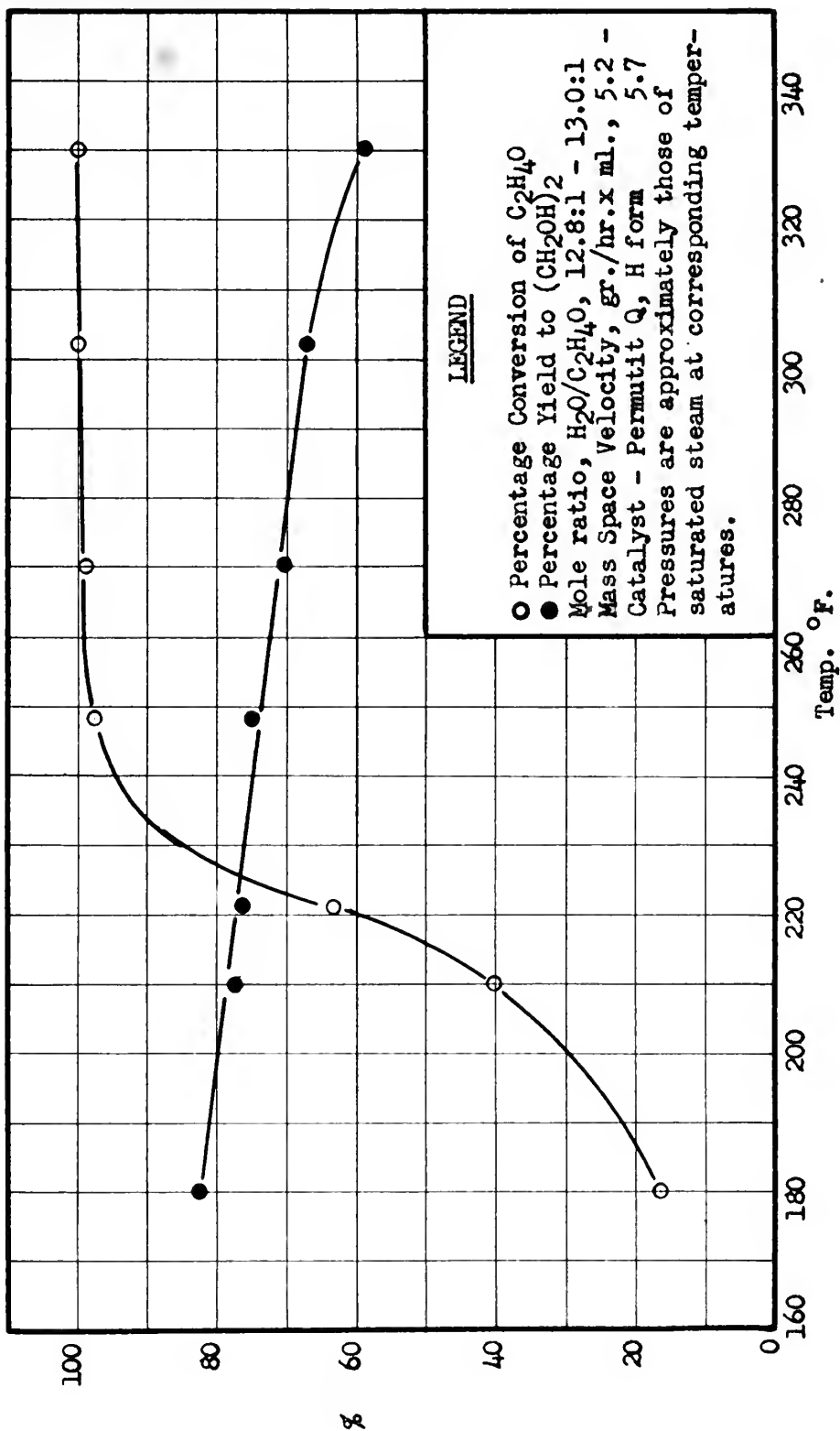


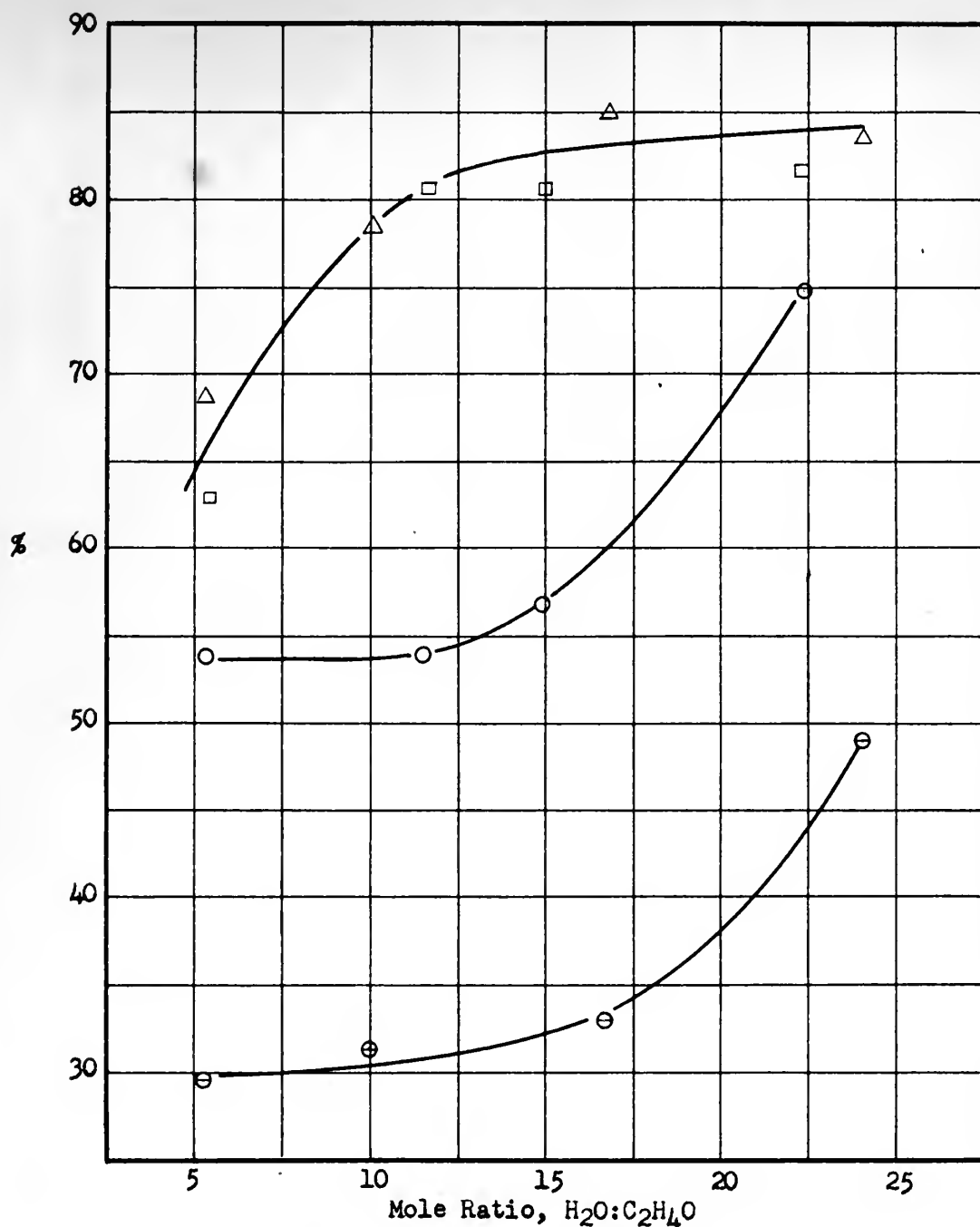
FIGURE 6

COMBINED EFFECT OF TEMPERATURE AND PRESSURE ON
 THE PERCENTAGE YIELD AND PERCENTAGE CONVERSION

velocity was chosen to give a wide range of conversions over the available temperature range and the mole ratio of near 13 to 1 was chosen to give high yields. The yield declined slowly from 82.5% at 180°F. to 68% at 300°F. and fell rapidly to 55% at 330°F. The percentage conversion increased rapidly from 16.6% at 180°F. to near complete conversion at 250°F.

3. Effect of Mole Ratio, $H_2O:C_2H_4O$

The effect of the mole ratio, $H_2O:C_2H_4O$, on the yield is shown in Figure 7. The temperature and pressure was held constant within a few degrees for these runs. It was intended initially to maintain a constant total mass space velocity, although this proved unsuccessful. In order to vary the mole ratio over a suitable range and maintain a constant total mass space velocity, it was necessary to vary greatly the mass space velocity of the ethylene oxide. It resulted in obtaining inconsistent data. The effect of varying the mass space velocity of the ethylene oxide apparently exceeded the mole ratio effect. Therefore, the ethylene oxide rate was maintained constant and the mole ratio varied by varying the water rate and consequently the total mass space velocity.



LEGEND

Δ % Yield at C_2H_4O Rate of 0.94 - 1.04 gr./hr. x ml.
 \square % Yield at C_2H_4O Rate of 0.50 - 0.53 gr./hr. x ml.
 \ominus % Conversion at C_2H_4O Rate of 0.94 - 1.04 gr./hr. x ml.
 \circ % Conversion at C_2H_4O Rate of 0.50 - 0.53 gr./hr. x ml.
 Catalyst, Permutit Q - H form
 Temperature Range $203^\circ F.$ - $211^\circ F.$

FIGURE 7

MOLE RATIO EFFECT ON PERCENTAGE YIELD
 AND PERCENTAGE CONVERSION

CHAPTER V

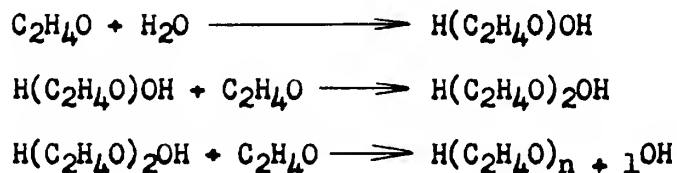
DISCUSSION OF RESULTS

A. Preliminary Data

The preliminary data served only to define the problem and supply information for the design of the pilot plant. It established sulfonic exchange materials in the hydrogen form as effective catalysts for the reaction. A life test gave no reduction in activity after twelve hours operation, which indicates the life of catalyst will be satisfactory. No poisoning effect occurred from the corrosion products in the wrought iron piping system, which permits the use of structural steel in plant equipment without the danger of poisoning the catalyst. Regeneration of the catalyst was unnecessary; however, if after continued use of a catalyst it should remove sufficient cations from the system to reduce its activity, regeneration with any acid would be a simple procedure. The analytical procedure does not justify the use of this data in the final study. The assumption that glycols higher than the dimer did not exist in appreciable amounts was erroneous. The yields and conversions based on this assumption were high and could not be verified in future work. The yield of 93.5% noted in Run No. 6 could not be duplicated and it is assumed to be in error.

B. Phase Conditions

The data obtained with the pilot plant indicate that in the vapor phase the ion exchange materials, Permutit Q and Zeo Karb, give yields of approximately 50% at mole ratios in excess of 10:1 and pressures between 5 and 10 psig. This low yield may be explained by the law of mass action. Assuming that the ion exchange material does not preferentially catalyze any of the reactions, they will proceed in accordance with the concentration of the reactants and the corresponding reaction rate constants. The reactions of interest are the following:



The concentration of ethylene oxide would not preferentially affect any of the reactions, as ethylene oxide takes part equally in all the reactions. A high yield of ethylene glycol, therefore, depends on a high concentration of water and a low concentration of the glycols. Solid catalysts may function by adsorbing the reactants on the surface where the reaction occurs. Gases adsorbing on the surface of materials are considered to condense and those gases with a higher boiling temperature condense more readily. It is therefore assumed that in a gaseous mixture of glycols, water and ethylene oxide, preferential adsorption would occur in the order named. The resulting concentration of glycols on the surface of the catalyst will be many times the concentration in the main body of the gases. Preferential adsorption

of the glycols would not occur appreciably if the catalyst is surrounded by an aqueous solution of glycols, as glycols do not materially lower the surface tension of water.

Regardless of the explanation, the data prove conclusively that Permutit Q and Zeo Karb are unsatisfactory in producing high yields of glycol when the reaction occurs in the vapor phase. While further work in the vapor phase was not considered, it should not be concluded that the vapor phase reaction should be discarded. The evidence of AlF_3 (17) catalyzing this reaction and producing high yields lends sufficient reason that other catalysts can accomplish similar or even superior results.

C. Mole Ratio Effect on Percentage Yield and Percentage Conversion

The mole ratio of reactants, water to ethylene oxide, has been found to greatly influence the yield and conversion of glycol. This effect is shown in Figure 7 over a range of ratios from 5:1 to 25:1. It would have been desirable to extend this range down to near 1; however, this was not possible. The heat of reaction, assuming the only product is ethylene glycol, is sufficient to vaporize all the products at a mole ratio of 2.7. An attempt to operate at a mole ratio of 3 gave inconsistent results, as the heat of reaction no doubt caused most of the products to vaporize and the reaction likely occurred partially in the vapor phase. The lower limit of 5:1 still is adequate to indicate the marked influence of excess water on the percentage yield. The percentage yields in Figure 7 conform closely to those

reported by Davis et al (2) and Matignon et al (13) in the mole ratio range between 5 and 15. Above 15, little, if any, increase is noted in this study while the references indicated a continued increase. A maximum yield of about 84% was obtained while Davis et al reported a yield of 93% at a mole ratio of 18.5:1 in an uncatalyzed reaction.

D. Temperature and Pressure Effect

The combined effect of temperature and pressure on the percentage yield is shown in Figure 6. The catalyst for this data was Permutit Q in the acid form with a 12 inch bed depth. The mass space velocity of the ethylene oxide was specifically chosen to give a wide range of conversions. Complete conversion occurred at about 250°F. while conversion was 16.6% at 180°F. A mole ratio of near 13:1 was chosen as this ratio produced near maximum yields and furthermore, in this range, the yield is quite insensitive to mole ratio variations. Exact control of the mole ratio was not possible because of the inherent errors in the rotameters, and, therefore, it was desirable to operate in an insensitive region.

The percentage yield was found to be a linear function of temperature between 180°F. and 300°F., dropping one per cent for every 8.5°F. increase in temperature. Above 300°F. the drop in percentage yield was more rapid. In the run at 330°F. products were formed that decomposed during distillation. Decomposition was noticed after the ethylene glycol fraction, as evidenced by a sharp decline in temperature and the collection of material in the dry ice trap. No attempt

was made to analyze the decomposition products as the information would have contributed little to the study. It can be postulated that high boiling aldehydes were formed which reacted with the glycols at the higher temperature producing dioxolanes and releasing water as a decomposition product.

The choice of temperature and pressure for operation of a commercial unit will depend on a very delicate economic balance. Yield is, of course, the major concern, as the by-products are of lower value than the ethylene glycol. Recycling of unreacted ethylene oxide is a minor problem, as the greater portion of it will pass from the reactor in the vapor phase. That portion of the ethylene oxide remaining dissolved in the solution of glycols will be removed in the initial phase of the purification process. The optimum temperature will involve a balance of operating and equipment costs versus the increased yield, with due consideration for by-products. However, it appears that a temperature between 200°F. and 230°F. would be optimum, and, since temperatures below 212°F. involve vacuum equipment, a more limited range of 212°F. to 230°F. seems appropriate.

E. Mass Space Velocity

The mass space velocity of the ethylene oxide or of the material passing through the reactor had no significant effect on the yield. This is shown in Figure 7. It is noted that a single curve represents the yield, while two curves represent the percentage conversion at the different mass space velocities of ethylene oxide.

The increased conversion at the high mole ratios is not readily explained. Assuming a constant mole ratio of water to ethylene oxide or its equivalent in glycols throughout the reactor, then the contact time would be greatly reduced at the higher mole ratios. Consider runs 28A and 32A. On the above assumption, contact times would be in the ratio of 2.9 to 10.7 respectively, which would indicate a much higher conversion for run 32A. Actually, the reverse is true, with a conversion of 49.0% for 28A and 29.5% for 32A.

In the heterogeneous system that exists, the reaction occurs at the interface of two phases. The reaction rate is controlled by mass transfer, or diffusion, of reactants to the interface and by the chemical reaction at the interface. If the rate of diffusion is slow relative to the chemical reaction, the overall rate will be controlled by diffusion and vice versa. These two factors vary independently with such variables as temperature and agitation. The reaction rate is greatly accelerated by an increase of temperature, while diffusion is affected to a minor degree. Agitation causes the diffusional rate to increase without affecting the reaction rate. Figure 6 indicates that the percentage conversion, and therefore the reaction rate, varies greatly with temperature in the range between 200°F. and 240°F. This shows that the chemical reaction is the controlling factor under these conditions. The increased turbulence, therefore, cannot explain the greater conversions at the higher mole ratios. This is further substantiated by the fact that the breaks in the percentage conversion curves of Figure 7 do not occur even near the same mass space velocities. The breaks would be expected to appear at near the same mass

space velocities if it were a matter of transition from streamline to turbulent flow.

The higher mole ratios would not materially affect the concentration of the water, as the large excess of water provides essentially a constant concentration. Furthermore, the reaction essentially goes to completion as the equilibrium constant at 100°C. is 1.1×10^7 (Appendix II). It appears that there is no simple explanation to the increased conversions at the higher mole ratios.

F. Reaction Rates

Reaction rate studies have largely been confined to homogeneous systems for the very good reason that the data from homogeneous reactions is more readily correlated into rate equations. Most significant in homogeneous reactions is that the rate is not a function of diffusivity. Furthermore, reaction times are known whether in a batch or flow system.

The study of solid catalyzed reactions becomes considerably more involved. Diffusion of the reactants and products to and away from the catalyst particle may become a controlling factor. This factor combined with the chemical reaction rate prevents any simple correlation. Diffusion may be the controlling rate factor under one set of conditions, while the chemical reaction may be limiting at other conditions. When the products and reactants, neglecting the solid catalyst, are homogeneous, the contact time is readily obtained from space velocities. When both liquid and gas phases exist the

space velocity term has no significance toward contact time, and reaction rate data cannot be obtained directly. In order that contact time can be determined in a heterogeneous system, it is necessary to know the reactor hold-up of each component. The equipment employed in this study was not suitable for determining column hold-up and therefore reaction rate constants are not considered.

CHAPTER VI

CONCLUSIONS

1. The reaction between ethylene oxide and water is readily catalyzed by ion exchange materials in either the hydroxyl or hydrogen form. All the strong cation and anion exchange resins were found to catalyze the reaction; however, the weak acid resins failed. The functional groups attached to the substrate are important in determining the catalytic activity, while the substrate has little, if any, influence. Ion exchange materials with sulfonic, phosphonic and strong amine groupings were found satisfactory, while the phenolic and carboxylic grouping failed to catalyze.

2. The reaction is catalyzed with strong cation and anion exchange resins in either the heterogeneous system of liquid and gas phases or in the homogeneous gas phase. However, the percentage yields obtained when operating in the gaseous phase were greatly reduced and are considered unsatisfactory. Percentage yields in the heterogeneous system were high, up to 86%, and are comparable to yields obtained when sulfuric acid is used.

3. Ion exchange materials of the strong acid and base types are satisfactory catalysts for the reaction between ethylene oxide and water, in which the catalyst does not contaminate the products and is suitable for continual reuse.

4. Ion exchange materials did not selectively catalyze the reaction between water and ethylene oxide. Percentage yields compare

closely to the uncatalyzed reaction.

5. The ion exchange materials did not solve the problem of obtaining ethylene glycol in a relatively concentrated form.

6. The mole ratio of the reactants water to ethylene oxide is the most significant factor in determining yields. A mole ratio of 10:1 is necessary to obtain yields of 80% and an even higher ratio is required to obtain a maximum of near 85%.

7. The combined effect of temperature and pressure greatly influence the reaction rate and the percentage yield. A temperature of 200°F. is necessary to obtain a substantial reaction rate and the rate increases rapidly up to 240°F. The percentage yield drops slowly with increasing temperature and pressure in the range between 180°F. and 250°F. and the corresponding pressures. Above a temperature of 300°F. the percentage yield drops rapidly with increasing temperature.



CHAPTER VII

RECOMMENDATIONS

1. Only the commercially available ion exchange resins were used in this study. It is recommended that a specific resin be developed in an effort to obtain a selective catalyst. The strong acid and base resins have proven very active catalysts, while the weak acid resin has proven ineffective. It is possible that some intermediate strength acidic or basic resin would be selective in its action. It is suggested that this can be accomplished by altering the functional group as well as the substrate. Various degrees of cross-linkage may change the catalytic characteristics of the resin.

2. The vapor phase hydration of ethylene oxide should be further explored. A selective catalyst that would function in the vapor phase would likely contribute greatly toward obtaining the ethylene glycol in a more concentrated form. Partial condensation of the products from a vapor phase reactor would yield a highly concentrated mixture of glycols.

3. Reaction rate data would be useful in scaling-up a reactor to commercial size. It is recommended that the equipment be redesigned to obtain hold-up in the reactor. The flow of materials could be stopped suddenly by means of quick acting valves installed in the feed lines. Immediately following the stoppage, an inert gas could be introduced to flush the reactants and products from the catalyst bed with a minimum of reaction occurring. An analysis of

the hold-up material would indicate the quantities and composition of each phase from which contact time could be estimated.

4. It is suggested that the upward flow of products and reactants through the catalyst bed might materially affect the reaction. The liquid would then tend to completely fill the void space in the bed rather than drain out as with the downward flow. The flow pattern of both phases would be completely altered with the thickness of the liquid film on the catalyst surface tending to increase. With upward flow a fluidized bed could also be investigated, which would provide still another flow pattern.

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APPENDIX I

SUPPLEMENTARY CATALYST DATA

<u>Catalyst</u>	<u>General Properties</u>	<u>Manufacturer</u>
Permutit Q	Cation Exchange Resin Sulfonated Polystyrene, Bead form Nuclear Sulfonic, --SO ₃ H Strong Acid Type Screen Analysis: Through 10 mesh, on 16 - 4% Through 16 mesh, on 20 - 15% Through 20 mesh, on 30 - 51% Through 30 mesh, on 40 - 21% Through 40 mesh, on 50 - 7% Through 50 mesh - 2% Density: Absolute 0.9 gr./ml. Apparent (wet) 0.425 gr./ml.	The Permutit Co., 330 West 42nd St., New York, N. Y.
Dowex 50	Cation Exchange Resin Sulfonated Polystyrene, bead form Nuclear Sulfonic, --SO ₃ H Strong Acid Type Particle size, 20-50 mesh Apparent Density (wet) 0.89 gr./ml. 9% Cross-linked	Dow Chemical Co., Midland, Michigan
Zeo Karb	Cation Exchange Material Sulfonated Coal, granular form Exchange groups, --SO ₃ H, --COOH, --OH Strong Acid Type Screen Analysis: Through 16 mesh, on 20 - 9% Through 20 mesh, on 30 - 29% Through 30 mesh, on 40 - 34% Through 40 mesh, on 50 - 23% Through 50 mesh - 5% Density: Absolute 0.725 gr./ml. Apparent (wet) 0.310 gr./ml.	The Permutit Co., 330 West 42nd St., New York, N. Y.

<u>Catalyst</u>	<u>General Properties</u>	<u>Manufacturer</u>
Zeo Rex	<p>Cation Exchange Resin Sulfonated Phenolic, granular form Exchange Groups, --SO₃H, --OH Strong Acid Type Screen Analysis: Through 16 mesh, on 20 - 10% Through 20 mesh, on 30 - 35% Through 30 mesh, on 40 - 28% Through 40 mesh, on 50 - 20% Through 50 mesh - 7% Absolute Density (wet) 1.579 gr./ml.</p>	<p>The Permutit Co., 330 West 42nd St., New York, N. Y.</p>
Permutit H	<p>Cation Exchange Resin Carboxylic acid resin, granular form Exchange groups, --COOH Weak Acid Type Screen Analysis: Through 10 mesh, on 16 - 2% Through 16 mesh, on 20 - 15% Through 20 mesh, on 30 - 52% Through 30 mesh, on 40 - 22% Through 40 mesh, on 50 - 7% Through 50 mesh - 2% Absolute Density (wet) 1.26 gr./ml.</p>	<p>The Permutit Co., 330 West 42nd St., New York, N. Y.</p>
Duolite C-60	<p>Cation Exchange Resin Polystyrene Resin, Bead form Nuclear phosphonic, --PO(OH)₂ Medium strength acid Particle size - 20 to 60 mesh Absolute Density 1.3 gr./ml.</p>	<p>Chemical Process Co., 901 Spring St., Redwood City, Calif.</p>
Permutit S	<p>Anion Exchange Resin Amine type, bead form Amine group - MH₂OH Strong base Screen Analysis: Through 10 mesh, on 16 - 2% Through 16 mesh, on 20 - 15% Through 20 mesh, on 30 - 54% Through 30 mesh, on 40 - 23% Through 40 mesh, on 50 - 5% Through 50 mesh - 1% Absolute Density (wet) 1.11 gr./ml.</p>	<p>The Permutit Co., 330 West 42nd St., New York, N. Y.</p>

APPENDIX II

LIQUID PHASE EQUILIBRIUM

The equilibrium constant for the reaction $C_2H_4O(lq.) + H_2O(lq.) \longrightarrow (CH_2OH)_2(lq.)$ as calculated from thermodynamic data is shown below:

$$\Delta H \text{ at } 298^\circ K. \text{ is } -17,390 \text{ cal./gr. mole (31)}$$

The absolute entropies of the reactants and products at $298^\circ C.$ are as follows:

$$S_{H_2O(lq.)} \text{ at } 298^\circ K. = 16.75 \text{ E.U./gr. mole (30)}$$

$$S_{C_2H_4O(lq.)} \text{ at } 298^\circ K. = 37.52 \text{ E.U./gr. mole (32)}$$

$$S_{(CH_2OH)_2(lq.)} \text{ at } 298^\circ K. = 39.9 \text{ E.U./gr. mole (33)}$$

$$S = 39.9 - (37.52 + 16.75) = -14.37 \text{ E.U./gr. mole}$$

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta F^\circ = -17,390 - 298 (-14.37)$$

$$= -13,110 \text{ cal./gr. mole}$$

$$\Delta F^\circ = -RT \ln K$$

$$\ln K = - \frac{1.987 \times 298}{-13,110}$$

$$K = 4.17 \times 10^9 \text{ at } 298^\circ K.$$

Assuming ΔH constant, the equilibrium constant at $373^\circ K.$ is computed from the following equation:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{K}{4.17 \times 10^9} = \frac{17,390}{1.987} \left[\frac{1}{373} - \frac{1}{298} \right]$$

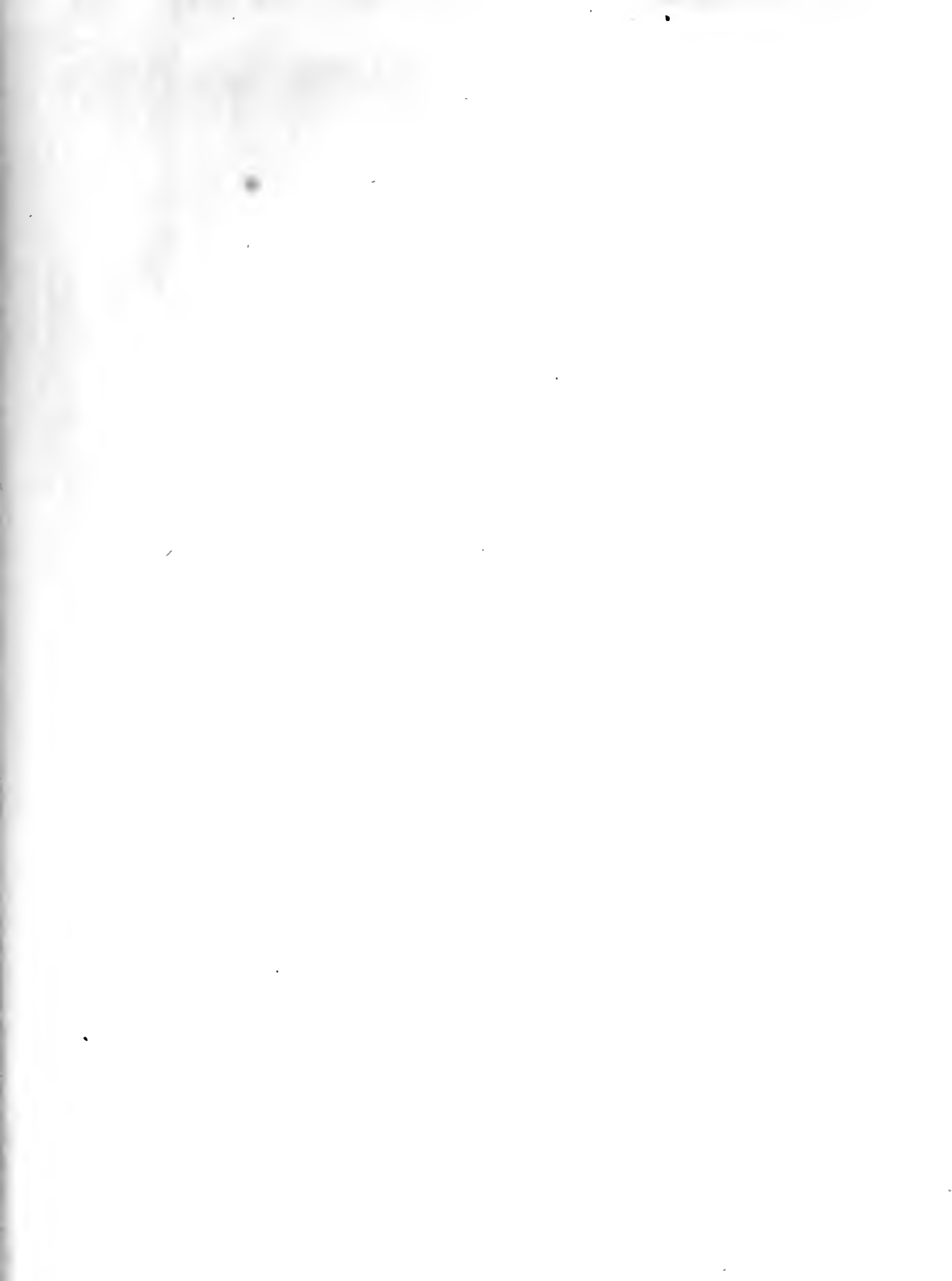
$$\ln \frac{K}{4.17 \times 10^9} = -5.9$$

$$K_{373^\circ K.} = 1.1 \times 10^7$$

VITA

The author, Leland McCulloch Reed, was born at Opheim, Montana, on September 19, 1917, the son of Charles Henry and Gertrude Ellen Reed. He attended elementary grades and high school at Opheim and graduated at the age of fifteen as valedictorian of his class. His formal education continued as a physics major at the College of Puget Sound, Tacoma, Washington, during the three academic years 1934 - 1937. His undergraduate education was completed at Montana State College where he attended two years and received a Bachelor of Science degree in Chemical Engineering in June of 1940. Virginia Polytechnic Institute of Blacksburg, Virginia, awarded the author a Teaching Fellowship where he received his Master of Science degree in Chemical Engineering in June of 1941. During his attendance at Montana State College he was elected to the honorary fraternities of Tau Beta Pi and Phi Kappa Phi. At Virginia Polytechnic Institute he was selected to membership in Phi Lambda Upsilon and associate membership in Sigma Xi. Following graduation he accepted employment with Shell Oil Company. In April of 1942 he resigned and accepted a civilian position with the United States Navy which led to assignment as a physicist in Brazil. He was commissioned an officer in the United States Navy in December of 1942 and has remained on active duty to date. He attended the United States Naval Postgraduate School, Annapolis, Maryland, during the academic year 1949 - 1950 followed by two years of graduate study in Chemical Engineering at Lehigh University, Bethlehem, Pennsylvania.





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